sodium metal–phenanthridine and sodium metal-6-phenylphenanthridine adducts in tetrahydrofuran were prepared (*ca.* 10^{-3}–10^{-4} *M*) and transferred to e.s.r. sample tubes by means of vacuum-line techniques.[37] The resulting sodium–phenanthridine solution was bright orange-red in color, while the sodium-6-phenylphenanthridine solution was deep green. The e.s.r. absorption spectra were taken on a spectrometer operating at 8996 Mc./sec. The magnetic field was modulated at 90 cycles/sec. Both with the phenanthridine and 6-phenylphenanthridine solutions the spectroscopic splitting factor or g.-value was 2.0054. By the use of phase sensitive detection the absorption spectra were presented as the first derivative of absorption with respect to field as a function of field. Both the sodium–phenanthridine and the sodium-6-phenylphenanthridine solutions gave pronounced, broad paramagnetic resonance absorption signals, definitely indicating the presence of free radical species. The lack of hyperfine components in the spectra of these samples seemed to be due to the transfer of electrons between the sodium–heterocycle adduct and unchanged heterocycle molecules present in the sample. Such electron transfer is known to obliterate hyperfine structure and result in a broadened absorption signal.[38] It was hoped that both higher conversion of the heterocycle into its 1:1 metal adduct and dilution of the sample would reveal hyperfine structure. With the phenanthridine samples this technique was successful. In this fashion a spectrum containing at least eight broad hyperfine components extending over a range of approximately 30 gauss was obtained. Subsequent measurements on more dilute samples indicated the presence of at least 16 components.

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(36) C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, **25**, 115 (1960).

(37) *Cf.* D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

(38) *Cf.* R. L. Ward and S. I. Weissman, *ibid.*, **76**, 3612 (1954), for an ingenious exploitation of such line broadening to determine the rate of electron transfer between the naphthalene radical–anion and naphthalene.

The Formation of Allenes from *gem*-Dihalocyclopropanes by Reaction with Alkyllithium Reagents[1,2]

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Several *gem*-dibromocyclopropanes, prepared by the addition of dibromocarbene to olefins, have been found to give allenes in high yields when treated with methyllithium or butyllithium in ether. The related dichloro compounds are inert to methyllithium but react slowly with butyllithium. In the cases considered there is no indication of carbene intermediates.

gem-Dihalocyclopropanes are readily available from the reaction of a dihalocarbene with an olefin, a reaction discovered by Doering and Hoffmann[4] in 1954 and widely employed by others since that time. Initially, these compounds were reported to be inert to most reagents and did not appear to have great synthetic utility.[5] Later, Doering and LaFlamme[7] found that treatment of certain *gem* dibromocyclopropanes with magnesium in ether gave allenes. The yields were not high (*ca.* 16–35%), but the allenes were reported to be essentially pure. The same investigators also found that these dibromides and the corresponding dichlorides reacted with high-surface sodium to give allenes in higher yields, accompanied, however, by isomers of the allenes.

In the search for a more efficient means to convert these dihalides to allenes, certain of which were desired for other studies, we examined the reaction of alkyllithium reagents with a number of *gem*-dihalocyclopropanes.[2]

Results and Discussion

Several *gem*-dibromocyclopropanes were prepared by the method of Doering and Hoffmann and all could be converted to allenes in good yields with either butyllithium or methyllithium (Table II, Experimental). Utilizing butyllithium in ether at −10°, cyclic and internal acyclic allenes were formed with no evidence of isomerization. In those cases in which terminal allenes were formed, the yields were lower and the allenes were extensively contaminated by materials which were assumed to be isomers of the allenes (based on gas chromatographic retention times). Subsequently, it was found that in these cases methyl-

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) Preliminary report, W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

(3) National Science Foundation Summer Fellow, 1959.

(4) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954), and later papers.

(5) The replacement of the halogen atoms by hydrogen by reduction with an active metal in a protonic solvent (ref. 4) appears to be a useful alternative to the Simmons–Smith reaction (ref. 6); *cf.*, K. Hofman, S. F. Orochena, S. M. Sax, and G. A. Jeffrey, *ibid.*, **81**, 992 (1959); S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).

(6) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(7) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

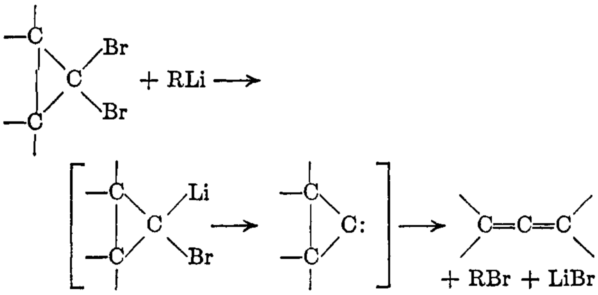
lithium in ether at −80° to 0° gave improved yields of allenes with no evidence of isomerization. This reagent serves equally well in the formation of internal allenes, both cyclic and acyclic. It is particularly convenient since it can be stored for long periods of time and does not lead to any side products which complicate purification of the allenes.[8] In all cases, an excess of the alkyllithium reagent was added to the dibromide while cooling to the desired temperature. No attempt was made to determine the optimum temperatures or concentrations of reagents since the initial results adequately demonstrated the utility of the reaction.

gem-Dichlorocyclopropanes appear to be inert to methyllithium but they do react with butyllithium. Thus 1,1-dichloro-2-hexylcyclopropane was recovered unchanged after treatment with methyllithium in refluxing ether, but gave 1,2-nonadiene in 31% yield (52% conversion) with butyllithium in ether at −10°. In refluxing ether, nearly complete isomerization of the allene occurred.

All of the allenes formed in this study were collected by preparative gas chromatography. 1,2-Cyclononadiene and 1,2-cyclodecadiene had been characterized previously[9] and were available for comparison. The structures of the other allenes were established by elemental analysis, characteristic infrared absorption at 1960–1980 cm.$^{-1}$, and oxidative ozonolysis followed by esterification to give the expected methyl esters.

The over-all conversion[7] of an olefin to an allene by the two-step sequence of the addition of dibromocarbene to the olefin[4] followed by reaction of the dibromide with an alkyllithium reagent[2] appears to be the best general method for synthesizing allenes. Subsequent to our initial description of the latter reaction,[2] Skatteböl[10] reported the conversion of a number of *gem*-dibromocyclopropanes to allenes in the same way, further demonstrating the utility of this method. In the conversion of the dibromides to allenes, neither high-surface sodium[7,11] nor magnesium[7,12] appear to offer any advantages as reagents. Isomerization of unsaturated compounds is always likely with the former[7,13] and the sluggish reactivity of the latter leads to relatively low yields. Furthermore, Logan[14] has reported that contrary to other reports,[7,12] allene–cyclopropane mixtures are obtained when magnesium is employed,[15] a mode of reaction which he also observed for *gem*-dichlorocyclopropanes when they were treated with magnesium and a reactive halide employed as an entraining agent.

The formation of carbenes from polyhalomethanes and alkyllithium reagents[16] suggests the intermediacy of carbenes in the formation of allenes:



However, treatment of 1,1-dibromo-2-methyl-3-propylcyclopropane with methyllithium in the presence of cyclohexene gave the expected allene in 88% yield with no indication of any trapping product. This result is not too surprising since the allenes which are formed could serve as trapping agents for carbenes[17] and no evidence for such products has been found. Thus if cyclopropylidenes are precursors of allenes, these carbenes must undergo valence isomerization to allenes far more rapidly than they add to olefins. The report by Jones[18] of the trapping of 2,2-diphenylcyclopropylidene, generated by decomposition of the related diazoalkane, takes on particular significance since this is a carbene which could isomerize to an unstrained allene, and Skatteböl[10] reported that the treatment of 2,2-dibromo-1,1-diphenylcyclopropane with methyllithium, a reaction which could give the same cyclopropylidene, gave only 1,1-diphenylallene.

In systems in which excessive strain would result upon formation of an allenic linkage, the possibility of intercepting carbene (or carbene-like) intermediates is greatly enhanced. We have reported such cases earlier[2,19] and will discuss related results in subsequent papers.

Experimental

General.—Infrared spectra were determined with a Perkin-Elmer Model 21 spectrophotometer (sodium chloride optics) employing carbon tetrachloride as a solvent. The gas chromatography apparatus (thermal conductivity detectors) utilized 0.5 × 170–200-cm. columns for analysis and 1 × 200-cm. columns for preparative purposes. The following liquid phases were employed (percentages by

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[8] Dr. T. J. Logan has informed us that commercially available butyllithium in *hexane* works equally well and apparently causes no isomerization of terminal allenes. In current work we have used butyllithium in hydrocarbons with success in a number of systems.

[9] W. R. Moore and R. C. Bertelson, *J. Org. Chem.*, **27**, 4182 (1962); R. C. Bertelson, doctoral dissertation, 1957.

[10] L. Skatteböl, *Tetrahedron Letters*, 167 (1961).

[11] W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 143 (1961).

[12] P. D. Gardner and M. Narayana, *J. Org. Chem.*, **26**, 3518 (1961).

[13] High-surface sodium has been employed as an active isomerizing agent for olefins; *cf.*, H. Pines and L. A. Schaap, "Advances in Catalysis, Volume XII," Academic Press, New York, N. Y., 1960; H. Pines and W. O. Haag, *J. Org. Chem.*, **23**, 328 (1958).

[14] T. J. Logan, *Tetrahedron Letters*, 173 (1961).

[15] The refractive index reported for 1,2-cyclononadiene in ref. 12 is very low and indicates that a mixture was at hand.

[16] (a) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959); (b) W. T. Miller, Jr., and C. S. Y. Kim, *ibid.*, **81**, 5008 (1959).

[17] W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 246 (1961).

[18] W. M. Jones, *J. Am. Chem. Soc.*, **82**, 6200 (1960).

[19] W. R. Moore, H. R. Ward, and R. F. Merritt, *ibid.*, **83**, 2019 (1961).

TABLE I

PREPARATION OF DIHALOCYCLOPROPANES

Olefin	Dihalo-cyclopropane	Yield, %	B.p. (mm.) or m.p., °C.	Formula	Carbon		Hydrogen	
					Calcd.	Found	Calcd.	Found
2-Hexene	(1)	56	62(3)	$C_7H_{12}Br_2$	32.84	33.00	4.71	4.96
1-Octene	(2)	43	87(2)	$C_9H_{16}Br_2$	38.06	38.88	5.68	5.89
1-Octene	(3)[a]	30	98(20)	$C_9H_{16}Cl_2$	55.39	55.59	8.27	8.22
1-Decene	(4)	35	95(0.4)	$C_{11}H_{20}Br_2$	42.32	42.42	6.46	6.52
cis-Cycloöctene	(5)	68	91(1)[b,c]	$C_9H_{14}Br_2$	...	...	...	...
cis-Cyclononene	(6)	95	100(0.2)[b]	$C_{10}H_{16}Br_2$	...	...	...	...
cis-Cyclodecene	(7)	93	48.5–49.5[d]	$C_{11}H_{18}Br_2$	42.61	42.89	5.84	5.93

[a] Prepared by W. F. Newell, B.S. thesis, Massachusetts Institute of Technology, 1956. [b] Micro short-path distillation the temperature is that of the heating bath. [c] Reported, ref. 12, b.p. 45° (0.15 mm.). [d] Recrystallized from ethanol.

TABLE II

ALLENES PREPARED FROM DIHALOCYCLOPROPANES

Dihalo-cyclopropane[a]	RLi	Allene[d]	Yield, %	Methyl ester[j]	ν^m cm.$^{-1}$	Formula	Carbon		Hydrogen	
							Calcd.	Found	Calcd.	Found
(1)	CH_3Li	2,3-Heptadiene[e]	88[i]	Butyrate[k]	1980	C_7H_{12}	87.42	87.52	12.58	12.60
(1)	C_4H_9Li	2,3-Heptadiene[e]	83							
(2)	CH_3Li	1,2-Nonadiene[e]	81	Heptanoate[k]	1970	C_9H_{16}	87.02	86.94	12.98	13.05
(2)	C_4H_9Li	1,2-Nonadiene[e]	49							
(3)	C_4H_9Li[b]	1,2-Nonadiene[e]	31							
(3)	C_4H_9Li[c]	1,2-Nonadiene[e]	Trace							
(4)	CH_3Li	1,2-Undecadiene[f]	68	Nonanoate[k]	1975	$C_{11}H_{20}$	86.76	86.77	13.24	13.04
(4)	C_4H_9Li	1,2-Undecadiene[f]	43							
(5)	CH_3Li	1,2-Cyclononadiene[g]	81		1957	C_9H_{14}[n]				
(6)	C_4H_9Li	1,2-Cyclodecadiene[h]	78		1962	$C_{10}H_{16}$[n]				
(7)	C_4H_9Li	1,2-Cycloundecadiene[h]	89	Sebacate[l]	1980	$C_{11}H_{18}$	87.92	87.81	12.08	12.12

[a] Table I. [b] Reaction at −10°. [c] Reaction in refluxing ether. [d] Allenes isolated by gas chromatography employing the indicated liquid phase and temperature. [e] NMPN, 40°. [f] NMPN, 87°. [g] NMPN, 70°. [h] C20M, 143°. [i] Employing cyclohexene–ether (1:1) as a solvent, an 88% yield of allene was obtained and no C_{13} products were found. [j] Obtained on oxidative ozonolysis and isolated by gas chromatography employing the indicated liquid phase and temperature. [k] C20M, 125°. [l] Dimethyl ester, S710, 236°; a minor product was also formed but was not investigated. [m] Medium-strong infrared absorption of allene. [n] Analysis and ozonolysis, ref. 9.

weight on 80–100 mesh Chromosorb): 25% of Union Carbide Chemical Corp. Carbowax 20 M (C20M), 15% of 3-nitro-3-methylpimelonitrile (NMPN) and 20% of Dow-Corning Silicone No. 710 (S710). Gas chromatographic analyses employed internal standards utilizing appropriate response factors with peak areas determined by planimetering. Elemental analyses were performed by Dr. S. M. Nagy and associates at the Massachusetts Institute of Technology and by the Scandinavian Microanalytical Laboratory. All melting points and boiling points are uncorrected.

1,1-Dibromocyclopropanes.[4]—All of these compounds were prepared by slurrying freshly-prepared alcohol-free potassium *t*-butoxide with a pentane solution of an olefin at −20° and slowly adding a pentane solution of bromoform. After hydrolysis and the usual work-up, the products were isolated by distillation. Analytical samples were further purified by gas chromatography or recrystallization. Yields (based on olefins as limiting reagents) and analytical data are summarized in Table I.

Preparation of Allenes.—The dibromocyclopropane was dissolved in ether under nitrogen and the solution was cooled to −10°. An excess of freshly prepared butyllithium in ether[20] was added dropwise with stirring. After an additional 10 min. at −10°, water was added cautiously. The ether layer was separated, washed several times with water, and dried over magnesium sulfate. The solvent was removed by distillation and the allene was isolated directly from the concentrate by gas chromatography.

When methyllithium was employed, the ether solution of the dibromide was cooled (temperatures ranging from 0 to −80° were employed) under nitrogen, and an excess of methyllithium in ether (stock solutions were prepared from methyl iodide and lithium and stored at 0°) was added dropwise with stirring. The reaction mixture was allowed to warm to room temperature and then was processed as above. Typical yields and analytical data are summarized in Table II.

Ozonolysis of Allenes.—Twenty microliters of an allene was dissolved in 10 ml. of methanol and ozone was passed through the solution for 5 min. Then 0.05 ml. of glacial acetic acid and 0.2 ml. of 30% hydrogen peroxide were added and the mixture was refluxed for 1 hr. A small amount of platinum black (to decompose peroxides) and a trace of hydrochloric acid (to catalyze esterification) were added. The solution was refluxed 3 hr., filtered, and concentrated by atmospheric distillation. The products were analyzed and isolated by gas chromatography. The esters produced (conditions are listed in the footnotes of Table II) were identified by comparison of gas chromatographic retention times and infrared spectra with those of authentic samples.

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(20) R. G. Jones, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 352.